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CRYSTAL FIELD INTERACTIONS OF "LARGE" ROTORS EMBEDDED IN SOLID PARAHYDROGEN (BRIEFING CHARTS AND ABSTRACT)

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BRIEFING CHARTS AND ABSTRACT

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14. ABSTRACT

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Matrix isolation has been used for many decades to study the structure and reactivity of species within an inert matrix. In most cases the infrared spectra of the dopants are fairly simple given that the rotational fine structure is usually frozen out by strong anisotropic interactions with the matrix host. In a few noteable cases, quantized rotation in the solid state has been observed spectroscopically, typically occuring when the rotational energy level spacings of the free rotor are large in comparison to the angle dependent barriers imposed by the host solid. The low angular anisotropy and weak interactions of solid parahydrogen has opened up the possibility to study the rotational motion of larger rotators and recently, we have reported that some molecules containing two second row elements, namely CO}, talk RG04 (2005)} and HCN,}, talk RD10 (2006)} do indeed undergo a hindered rotational motion within the parahydrogen matrix. \vspace {8pt} In this talk, we discuss our efforts to use infrared spectroscopy to study the rotational dynamics of relatively ``large" rotators embedded in solid parahydrogen, \emph{i.e.}~molecules that do not rotate in other solid matrices. Parahydrogen matrices containing $\sim 5-10 $ ppm of CO, NO, HCN, and HCCH are produced using the Rapid Vapor Deposition technique and probed with a high resolution FTIR absorption spectrometer. Analysis of the resulting ro-vibrational spectra show that the crystal field splittings are comparable to the rotational energy level spacings of the free rotor and are sensitive to the vibrational state of the molecule. We analyze this hindered rotational motion using the electrostatic formalism developed by Devonshire} \underline {A153}, 601 (1936).} and Flygare.}, \underline{44}, 1389 (1966).} Additionally, we examine the magnitude of the various crystal field parameters using ab initio H$_2$-dopant pair potential energy surfaces.

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Crystal Field Interactions of "Large" Rotors Embedded in Solid Parahydrogen

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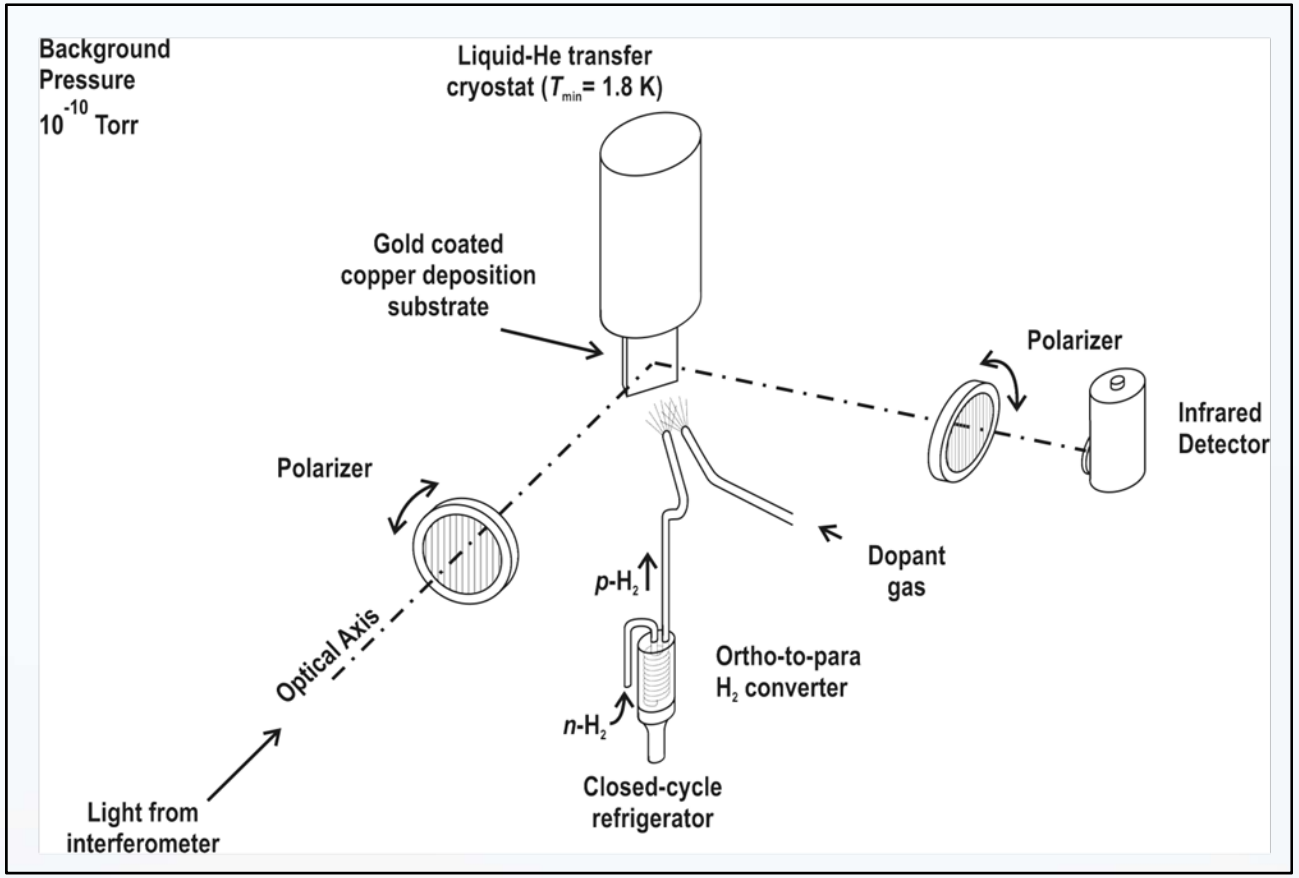
Rotation in the Solid Matrices

- Rare gas matrices and traditional molecular matrices:
  - Small hydrides: HX, H_2O, NH_2, NH_3, CH_3, CH_4
  - *Perhaps* ClF, CN (ESR and IR spectra conflict)
  - fcc lattice structure
- Solid Parahydrogen:
  - Very low angular anisotropy, and weak intermolecular interactions
  - Small hydrides: HX, H_2O, NH_3, CH_3, CH_4
  - "*Large*" molecules: N_2, O_2, CO, HCN, … *more*?
  - fcc (as deposited) and hcp (annealed) lattice structure

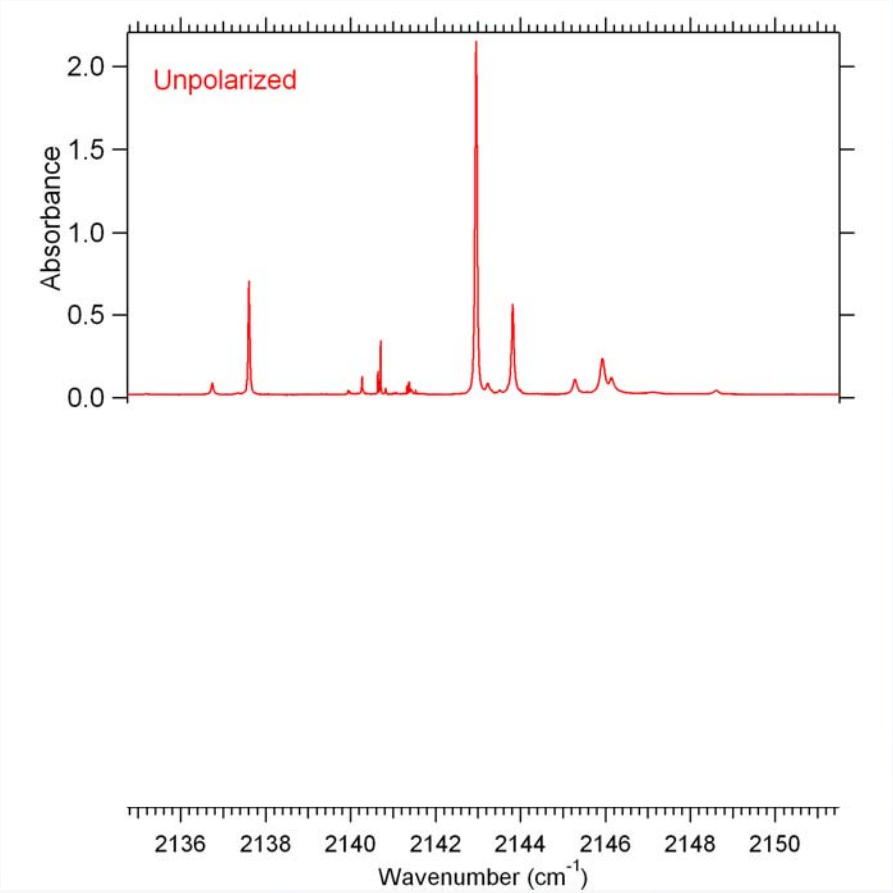
Narrow spectral lines widths and the ability to examine the rotation of larger molecules allows us to examine the impurity-matrix interactions with remarkable clarity

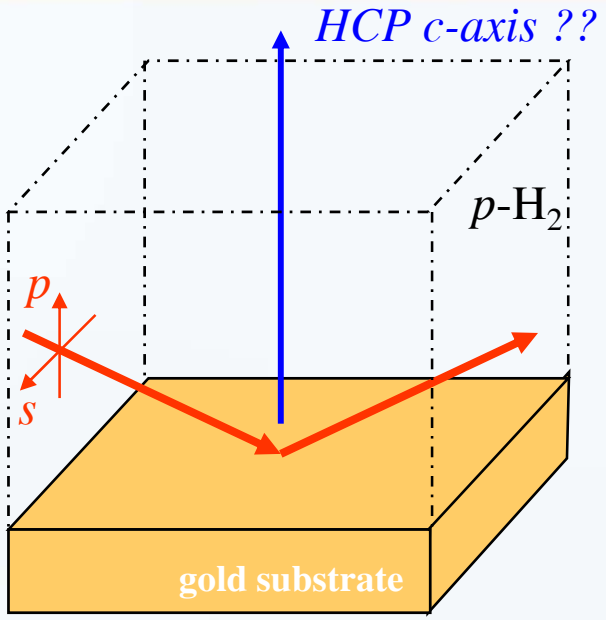
Rapid vapor deposition of p-H2

- Reflection based set-up (FTIR).
- [o-H_2] < 100 ppm.
- p-H_2 deposition rate ~150 mmol/hr → ~1 mm/hr thickness.
- Deposition at 2.3 K. Sample annealed at 4.3 K for 30 min.



Polarization Spectroscopy

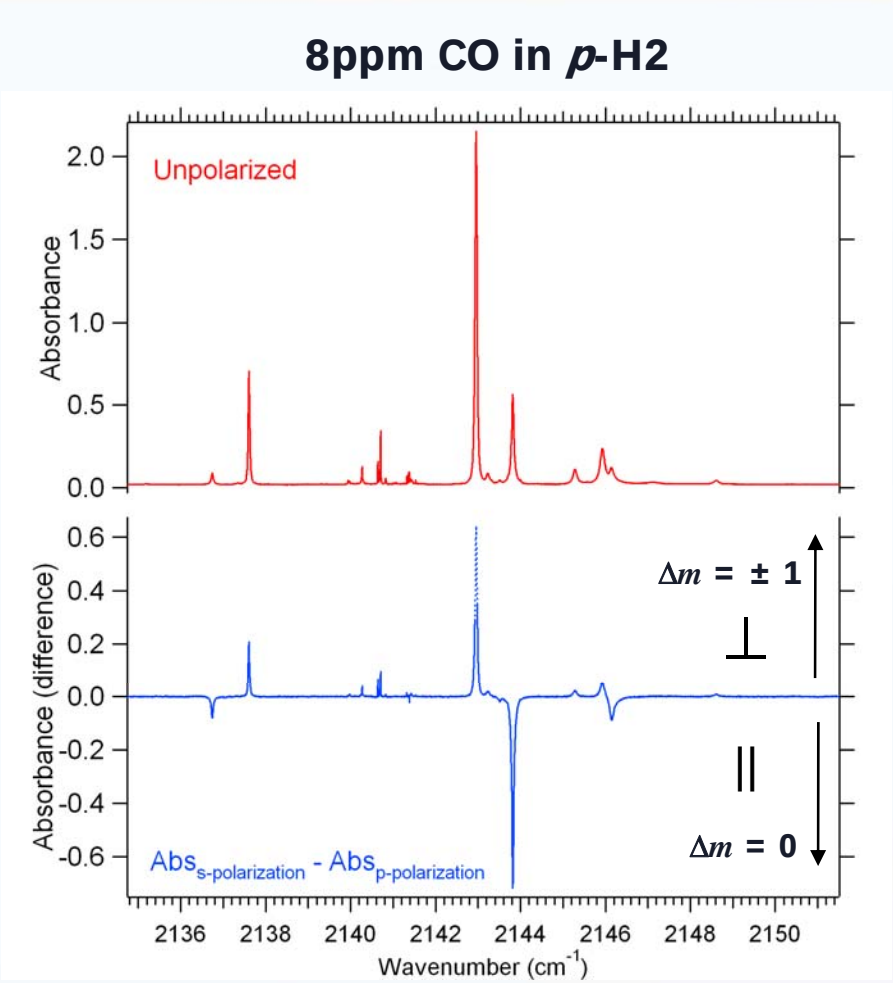


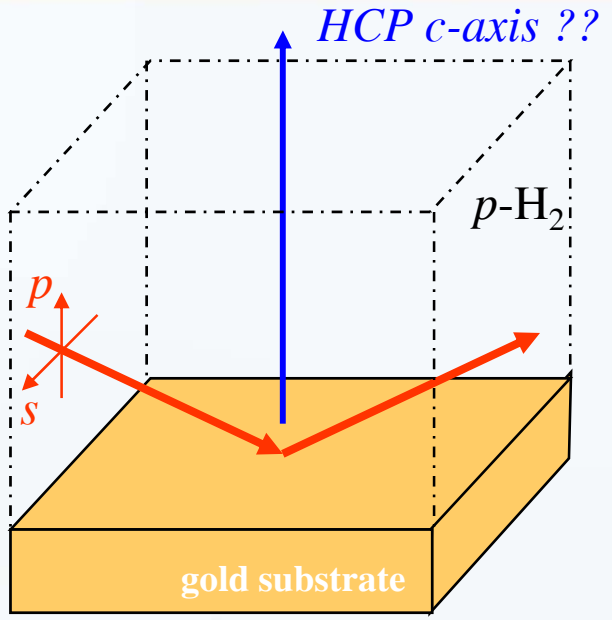


Polarization analysis provides:

- **An assignment of the perpendicular and parallel components to the crystal field perturbed rotational structure (*i.e.* Δm)**
- **$Abs_{s\text{-}pol} - Abs_{p\text{-}pol} = \frac{1}{2}\mu^2_{\perp} - \frac{1}{2}\mu^2_{\parallel}$**

Polarization Spectroscopy





Polarization analysis provides:

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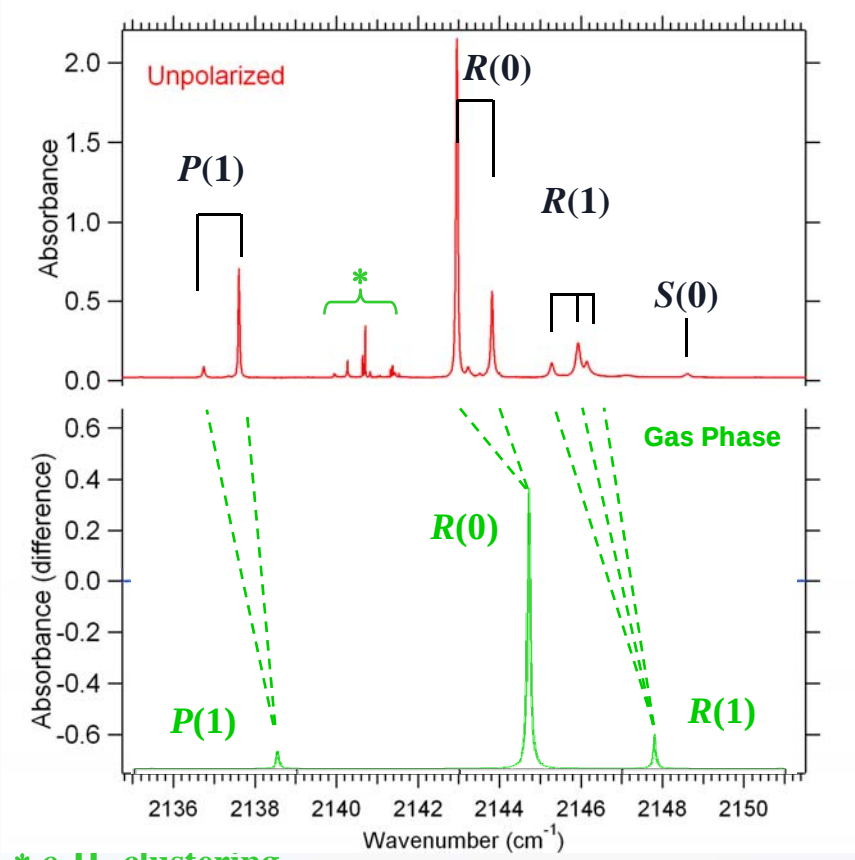
- **$Abs_{s\text{-}pol} - Abs_{p\text{-}pol} = \frac{1}{2}\mu^2_{\perp} - \frac{1}{2}\mu^2_{\parallel}$**

Rotation in parahydrogen

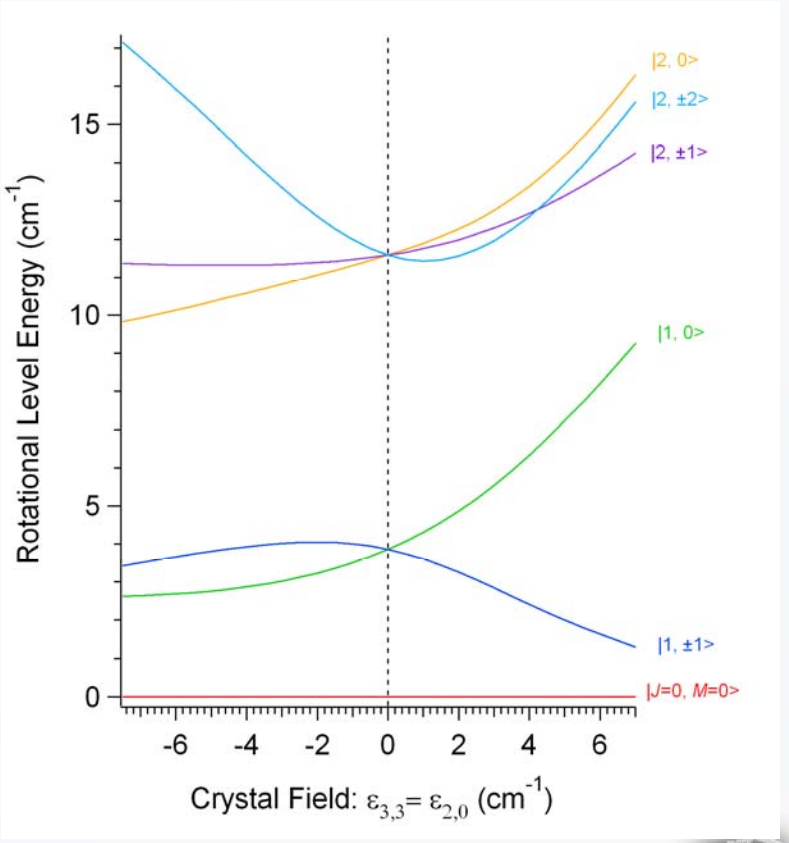
8 ppm CO in *p*-H_2



* *o*-H_2 clustering

Simulation:

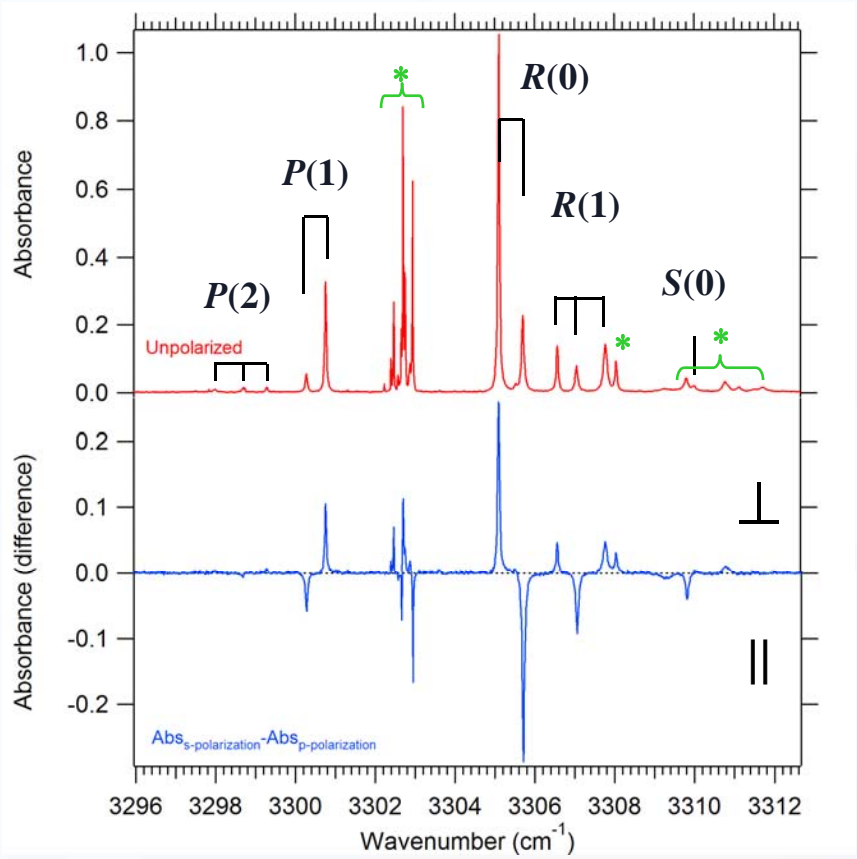
Linear molecule in *h.c.p* crystal field



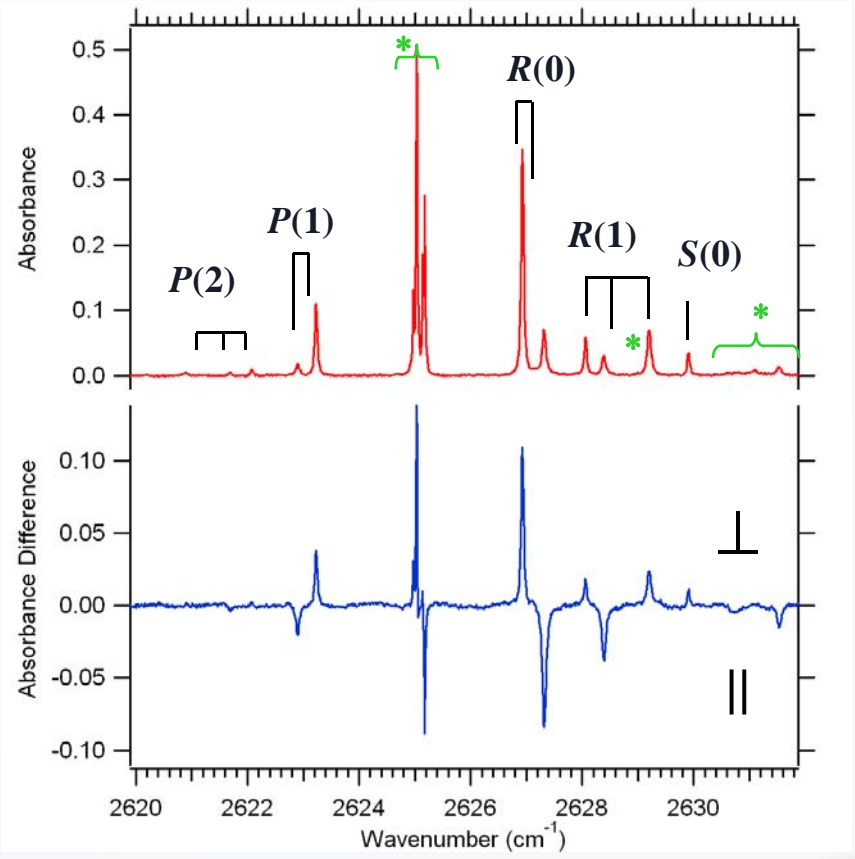
Simulation uses theory of: Devonshire, Proc. Roy. Soc. London A 153, 601 (1936); Bowers and Flygare, J. Chem. Phys., 44, 1389 (1966).

HCN in parahydrogen

8 ppm HCN in *p*-H_2

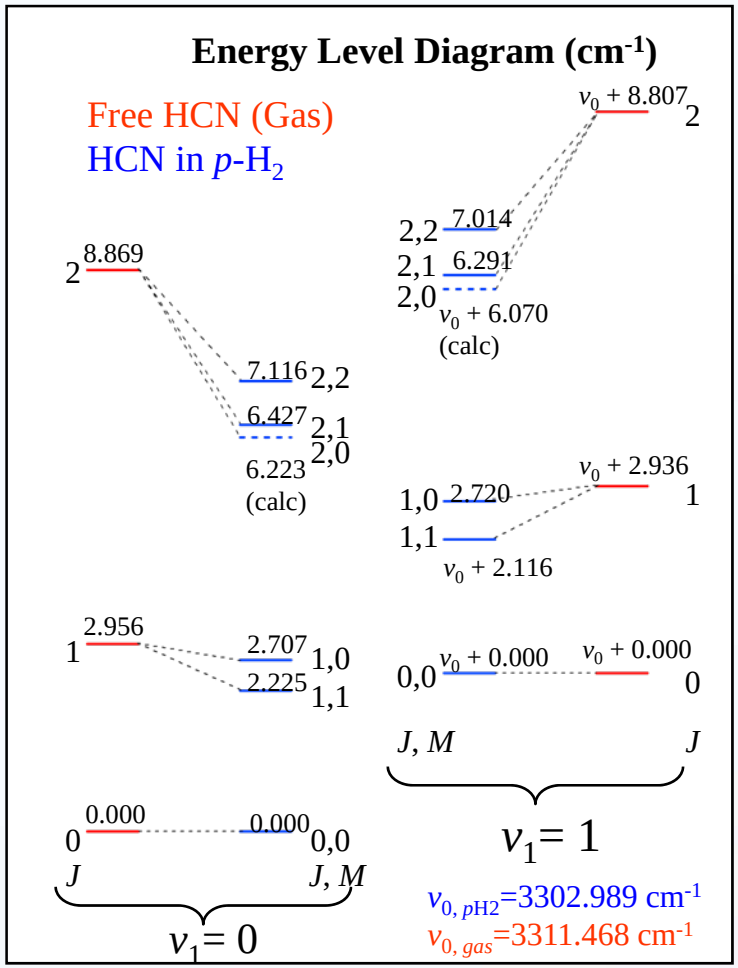


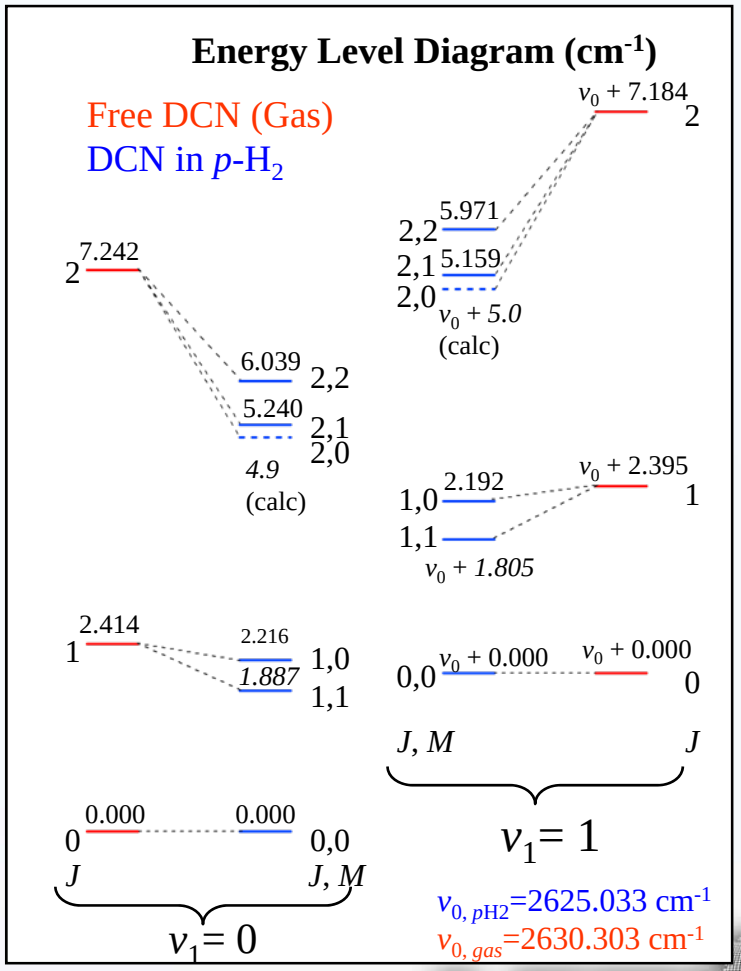
2 ppm DCN in *p*-H_2



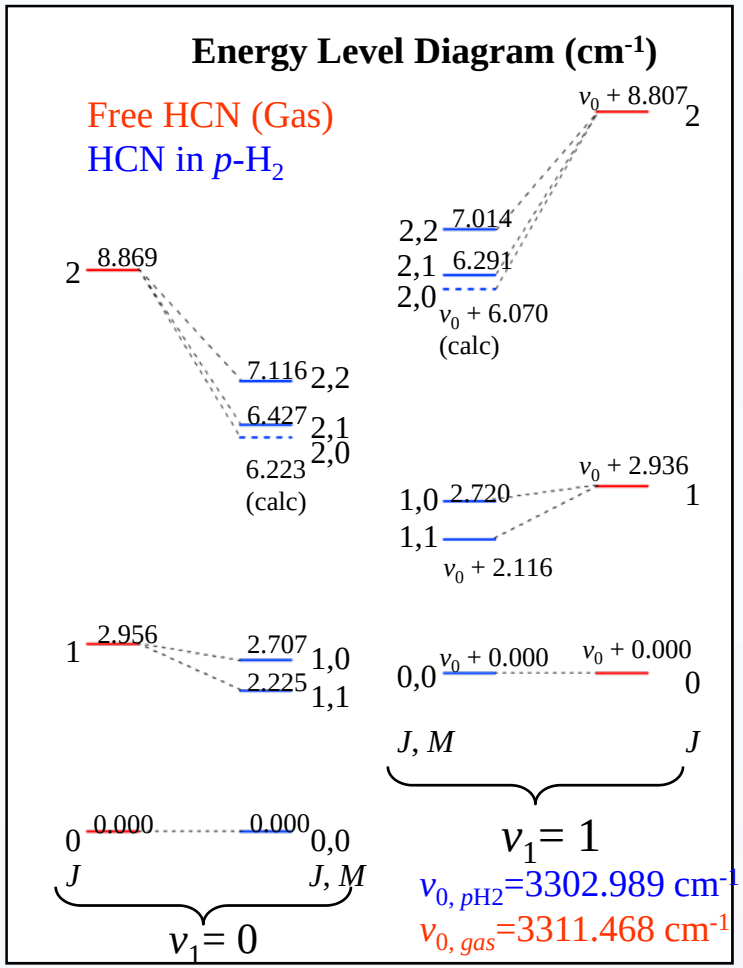
* *o*-H_2 clustering

HCN / DCN Energy Level Diagrams





Interpretation of the Rotational Fine Structure- HCN + DCN



Crystal field theory (linear molecule in HCP lattice) *

$H = H_{r,v} + V_{cry}$

$V_{cry} = \varepsilon_2 C_{2,0}(\Omega_{HCN}) + \varepsilon_3 [C_{3,-3}(\Omega_{HCN}) - C_{3,3}(\Omega_{HCN})]$

where $C_{l,m}(\Omega) = \left(\frac{4\pi}{2l+1}\right)^{1/2} Y_{l,m}(\Omega)$

"Fitting" Results in cm^{-1}: (10 levels, 9 parameters)

	HCN		DCN	
	p-H_2	Gas	p-H_2	Gas
B	1.475(5)	1.478	1.2791(5)	1.207
ΔB	-0.005(5)	-0.010	-0.032(5)	-0.010
D	0.0675(5)	2.910×10^{-6}	0.0654(5)	1.927×10^{-6}
ΔD	0.0032(5)	0.025×10^{-6}	-0.0028(5)	0.017×10^{-6}
ν_0	3302.989(5)	3311.4770	2625.093(10	2630.3033
ε_2	-1.274(5)	-	-2.142(5)	-
$\Delta\varepsilon_2$	-0.193(5)	-	-0.047(5)	-
ε_3	6.850(5)	-	7.500(5)	-
$\Delta\varepsilon_3$	0.767(5)	-	0.028(5)	-

Identical!

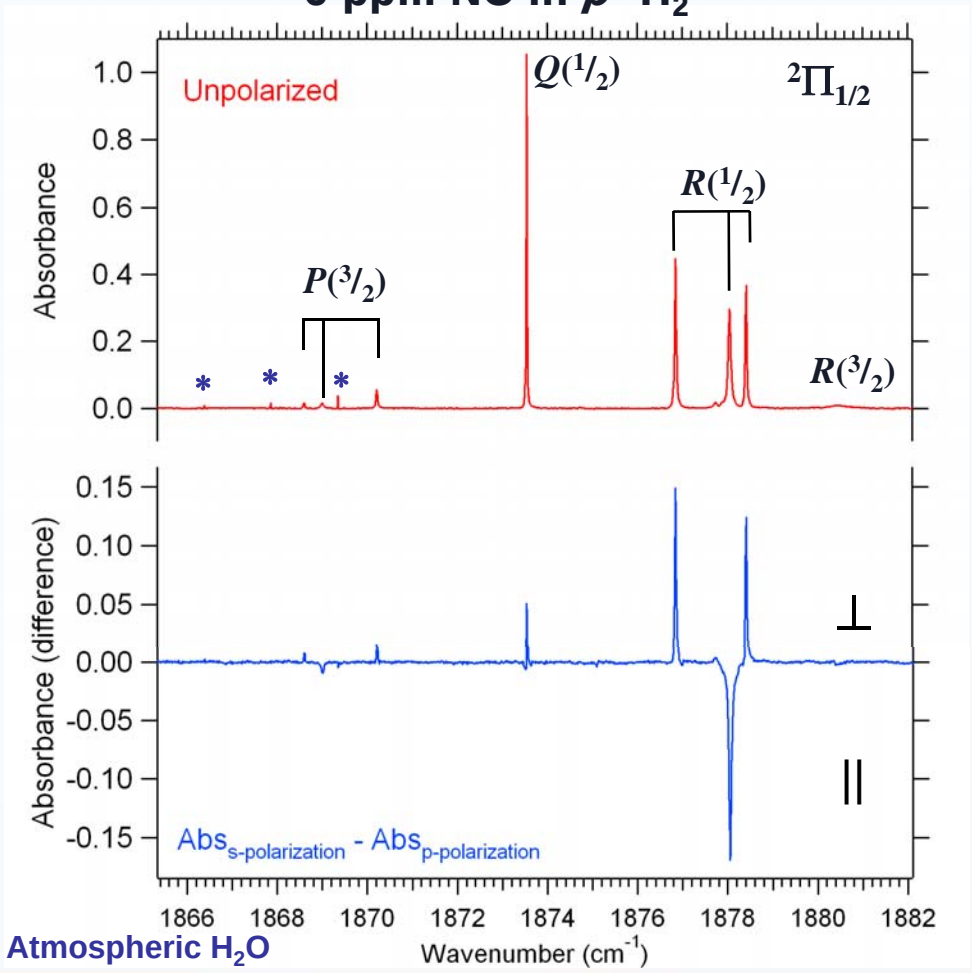
× 20,000!

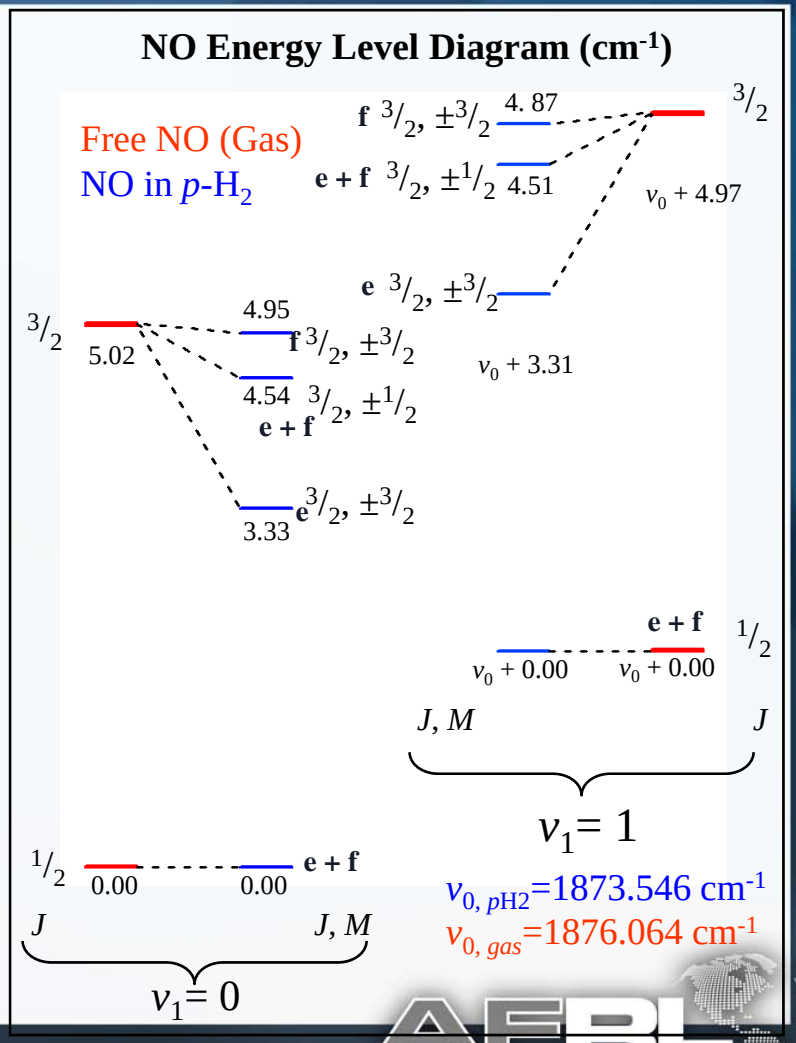
very large!

NOTE: Above perturbation does not converge for large D! Treatment was modified to incorporate centrifugal distortion after crystal field calculation to avoid this problem.

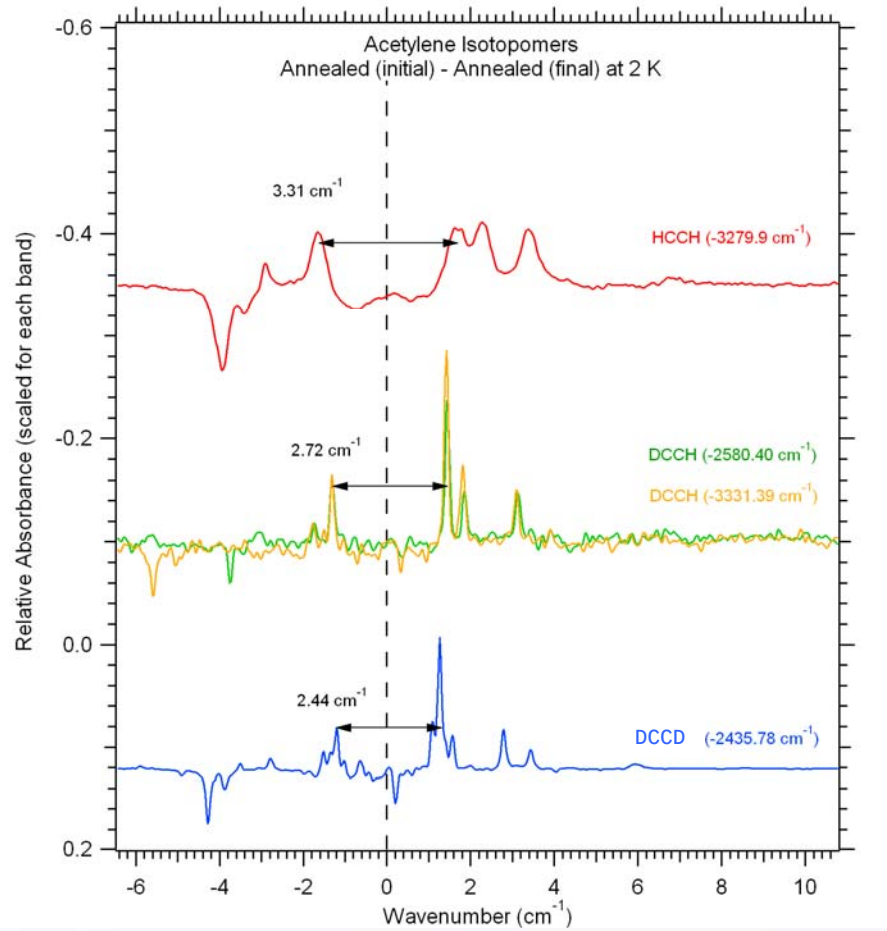
Devonshire, Proc. Roy. Soc. London A 153, 601 (1936); Bowers and Flygare, J. Chem. Phys., 44, 1389 (1966).

NO in Solid Parahydrogen





Preliminary C_2H_2 in parahydrogen



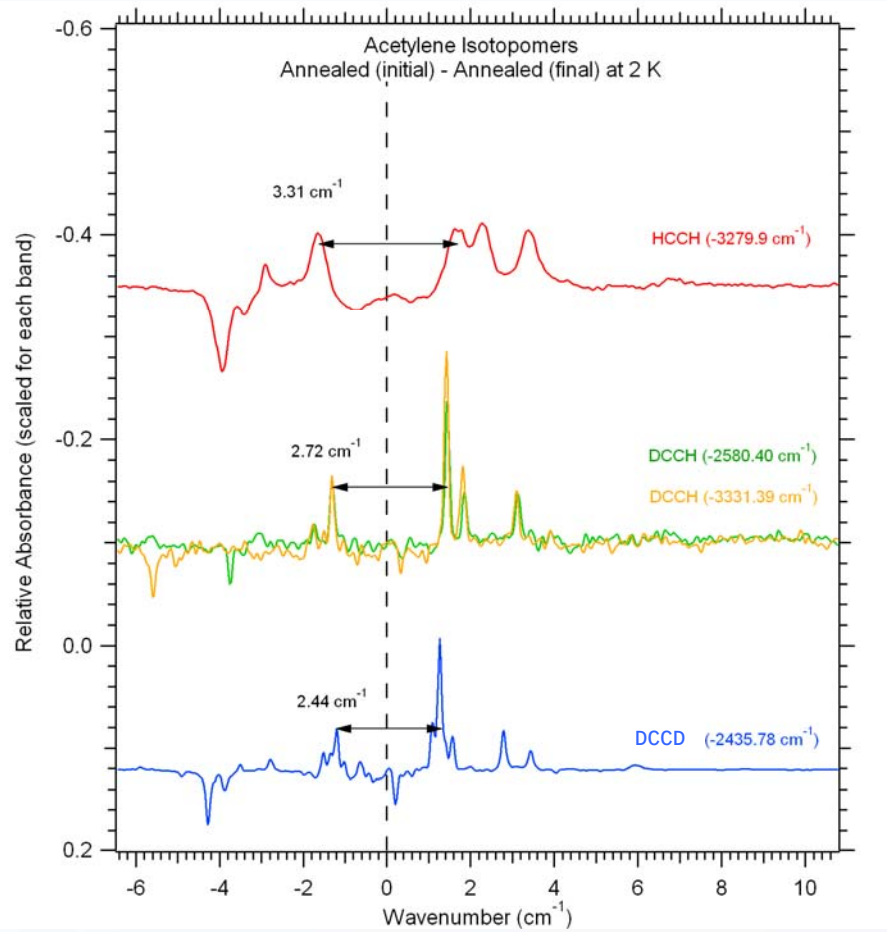
$E_{R(0)} - E_{P(1)}$ $(4B)$

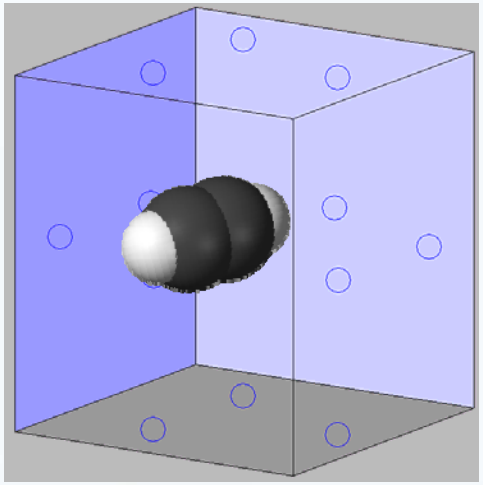
	Gas		pH_2	
	Wavenumer	Relative	Wavenumber	Relative
HCCH	4.71 cm^{-1}	**1.00**	3.35 cm^{-1}	**1**
DCCH	3.97 cm^{-1}	**0.84**	2.74 cm^{-1}	**0.82**
DCCD	3.39 cm^{-1}	**0.72**	2.47 cm^{-1}	**0.74**

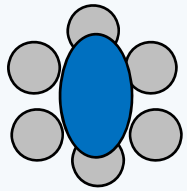
- Acetylene IR spectrum 'ages'... timescale of 30 minutes. Aging appears to be acetylene-acetylene clustering.
- "Rotational spectrum" disappears fairly quickly (but not with annealing!)

Y.P. Lee and collaborators *Chem. Phys. Lett.* 435 247-251 (2007) – no rotation at 'high' [o-H_2]

Preliminary C_2H_2 in parahydrogen



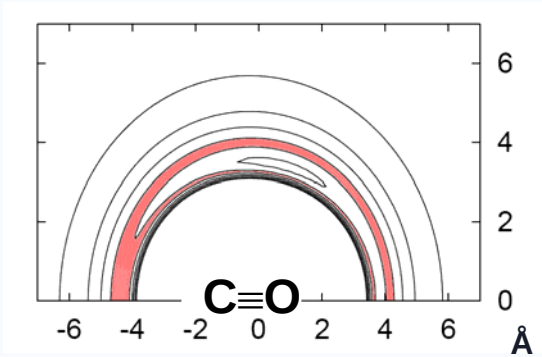




- HCCH Van der Waal diameter ~ 6.4 Å
- *p*-H_2 intermolecular spacing – 3.8 Å
- Substantial overlap of wavefunctions

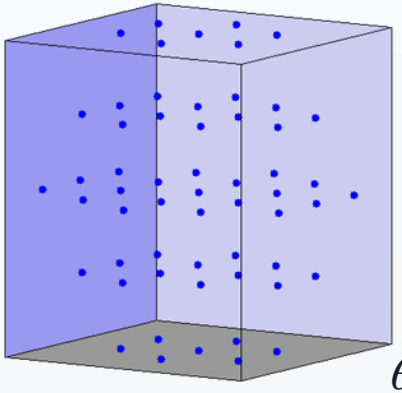
Prediction of Crystal Field Parameters: Truncation

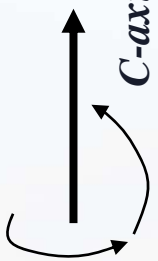
Pair Potential



+

H_2 – *h.c.p.* lattice

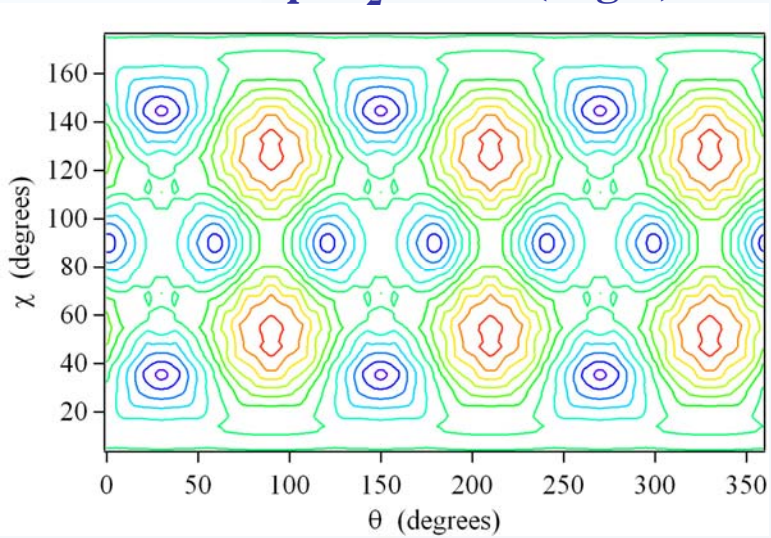




χ (*out-of plane*)

θ (*in-plane*)

Rotational PES dopant in *h.c.p* H_2 lattice (Rigid)



Crystal field theory (linear molecule in HCP lattice) *

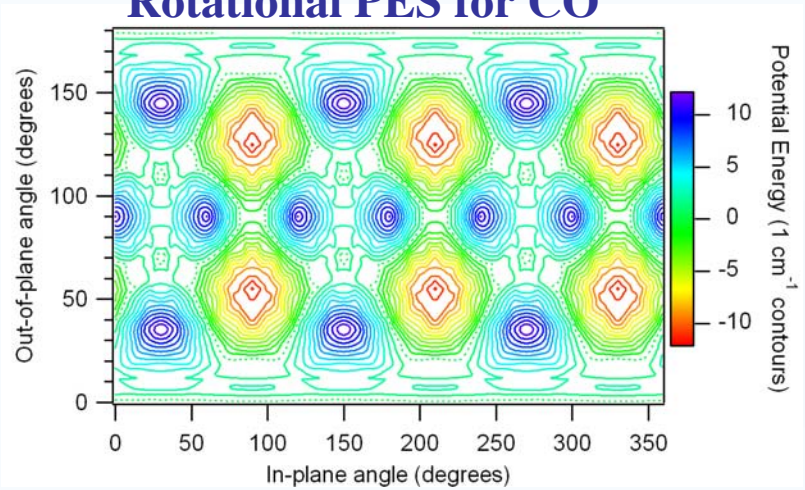
$$H = H_{r,v} + V_{cry}$$

$$V_{cry} = \sum_{l,m}^{m \le l} \varepsilon_{l,\pm m} \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_{l,\pm m}(\Omega)$$

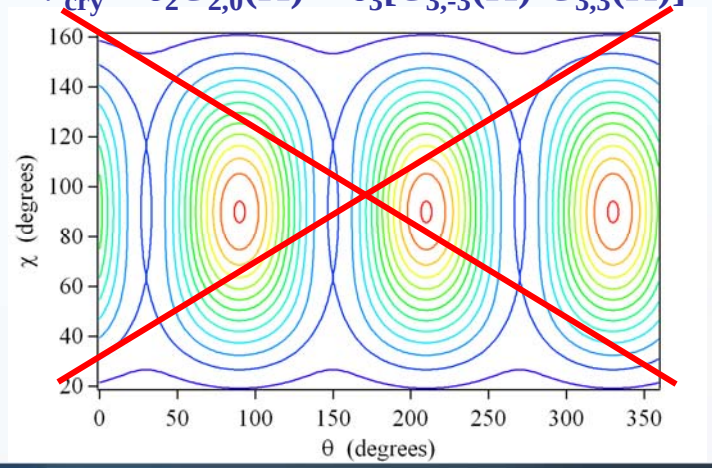
* SAPT / MC⁺BS, P. Jankowski and K. Szalwicz, *J. Chem. Phys.* 108, 3554 (1998).

Prediction of Crystal Field Parameters: Truncation - CO

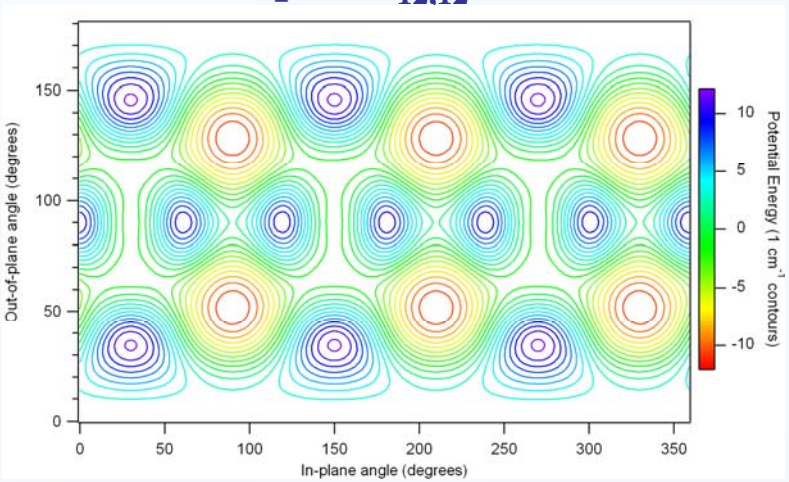
Rotational PES for CO



$V_{cry} = \varepsilon_2 C_{2,0}(\Omega) + \varepsilon_3[C_{3,-3}(\Omega) - C_{3,3}(\Omega)]$



CFT –up to $C_{12,12}(\Omega)$



(2.52)*

ε (cm^{-1})	Term	ε (cm^{-1})	Term
4.86	$C_{3,3}(\Omega)$	0.65	$C_{9,3}(\Omega)$
6.74	$C_{5,3}(\Omega)$	0.55	$C_{12,6}(\Omega)$
6.54	$C_{4,0}(\Omega)$	0.46	$C_{8,0}(\Omega)$
3.68	$C_{6,6}(\Omega)$	0.43	$C_{12,12}(\Omega)$
-5.80	$C_{6,0}(\Omega)$	-0.02	$C_{12,0}(\Omega)$
2.61	$C_{7,3}(\Omega)$	-0.47	$C_{11,3}(\Omega)$
1.10	$C_{8,6}(\Omega)$	-0.22	$C_{2,0}(\Omega)$

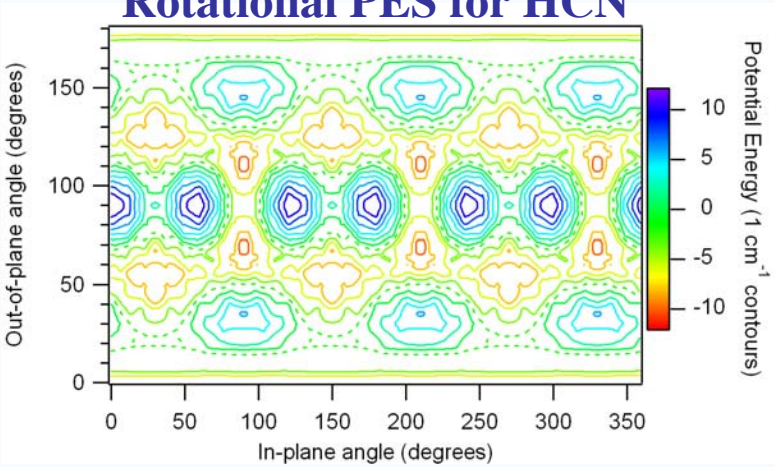
(1.03)*

* Experimentally fitted values.

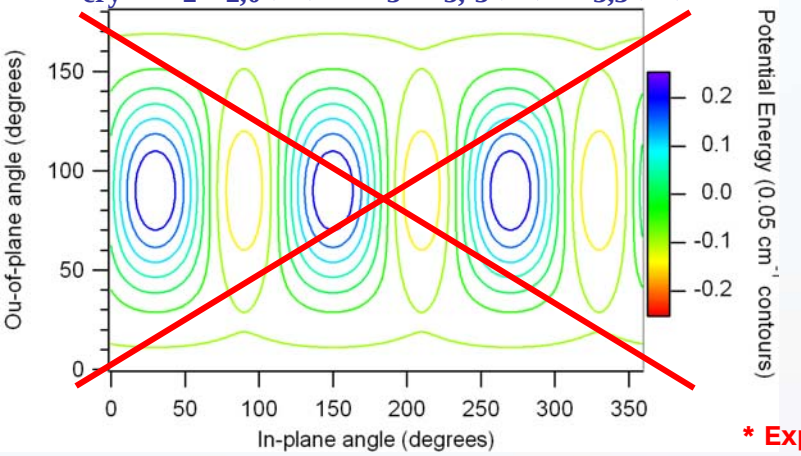
* CO-H_2 Pair Potential - SAPT/MC$^+$BS, P. Jankowski and K. Szalwicz, *J. Chem. Phys.* 108, 3554 (1998)

Prediction of Crystal Field Parameters: Truncation - HCN

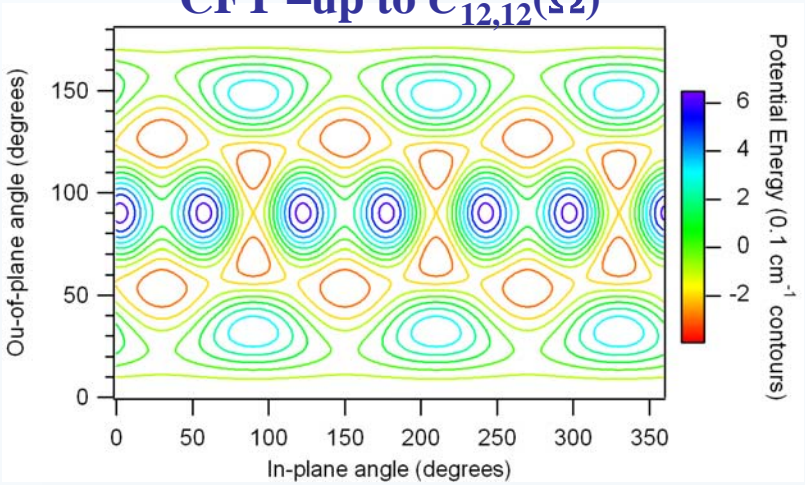
Rotational PES for HCN



$V_{cry} = \varepsilon_2 C_{2,0}(\Omega) + \varepsilon_3[C_{3,-3}(\Omega) - C_{3,3}(\Omega)]$



CFT –up to $C_{12,12}(\Omega)$

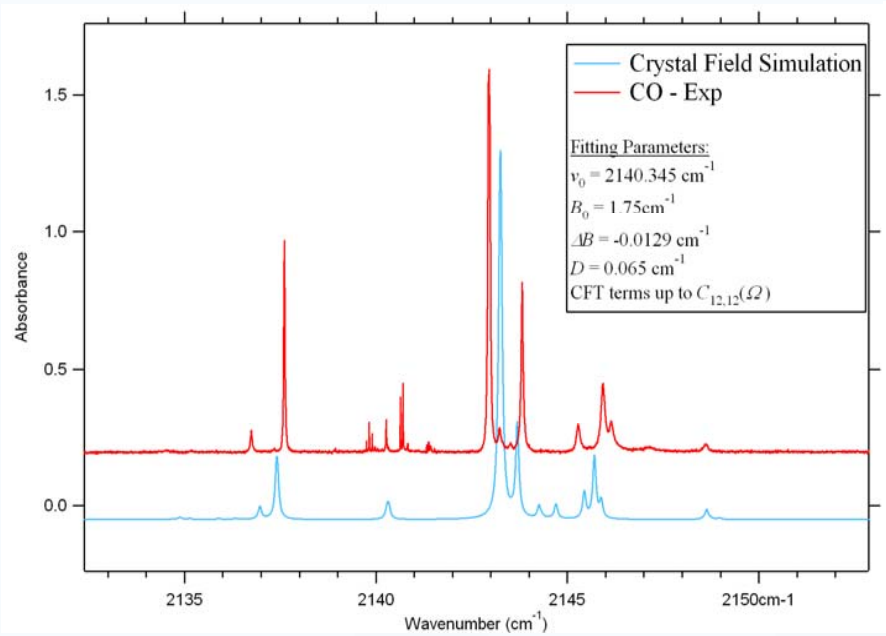


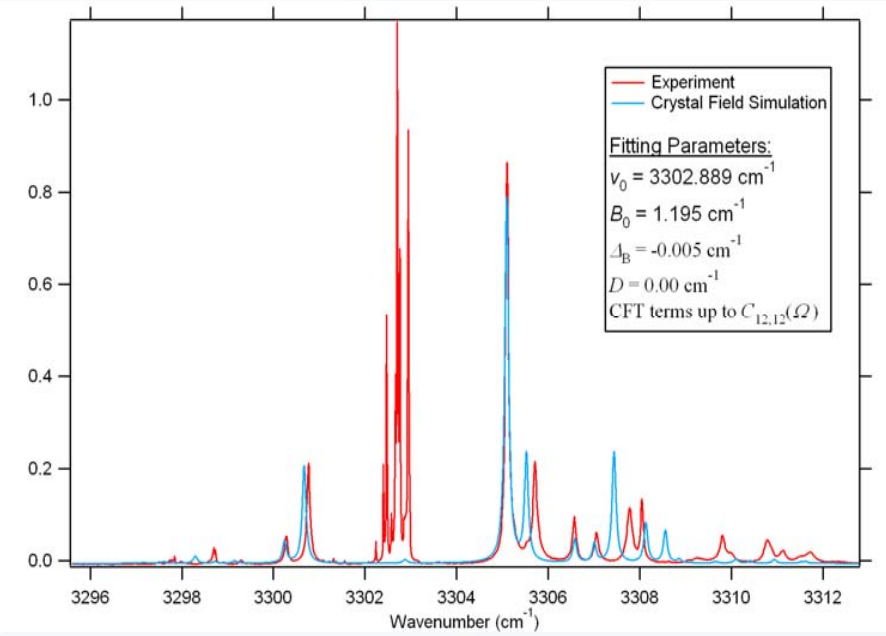
ε (cm^{-1})	Term	ε (cm^{-1})	Term
-3.04	$C_{6,6}(\Omega)$	0.63	$C_{8,6}(\Omega)$
-2.28	$C_{5,3}(\Omega)$	0.09	$C_{8,0}(\Omega)$
3.35	$C_{4,0}(\Omega)$	-0.01	$C_{9,3}(\Omega)$
-4.82	$C_{6,0}(\Omega)$		
0.70	$C_{3,3}(\Omega)$	(6.85/7.50)*	
-1.24	$C_{7,3}(\Omega)$		
-0.47	$C_{2,0}(\Omega)$	(-1.27/-2.14)*	

* Experimental fitted values for HCN/DCN.

* HCN-H_2 Pair Potential - D. Moore, unpublished,

Estimation of Crystal Field Parameters: Simulated Spectrum for CO + HCN





- Qualitative agreement with experiment
- Overestimates splittling in J=1 manifold – rigid lattice structure
- Underestimates $\varepsilon_{2,0}$ parameter
- Compression of rotational fine structure (B_{eff}/D$_{eff}$) not accounted for by crystal field

Summary

Conclusions

- Parahydrogen is remarkably accommodating to rotating molecules... even HCCH!
- “reduction” in rotational constant can be thought as a large centrifugal distortion constant... B may not be affected at all
- Simulations using pair potentials and rigid lattice agree qualitatively with experiment

Acknowledgements:

- Takamasa Momose (Crystal field theory for CO)
- David Anderson (NO data)
- David Moore (H_2-HCN potential calculations)

QUESTIONS?

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